Polyhedron 27 (2008) 1995–1998

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Monodentate *S-vs.* bidentate 1,5-*O*,*S*-coordination of *N*-phosphoryl-*N*′-(R)-thioureas with Pd(II)

Damir A. Safin [a,*], Felix D. Sokolov [a], Łukasz Szyrwiel [b], Sergey V. Baranov [a], Maria G. Babashkina [a], Timur R. Gimadiev [a], Henryk Kozlowski [b]

[a] *A.M. Butlerov Chemistry Institute, Kazan State University, Kremlevskaya Street 18, 420008 Kazan, Russian Federation*
[b] *Faculty of Chemistry, University of Wroclaw, F. Joliot-Curie Str. 14, 50383 Wroclaw, Poland*

ARTICLE INFO

Article history:
Received 26 February 2008
Accepted 14 March 2008
Available online 2 May 2008

Keywords:
Complex
Crown-ether
Monodentate coordination
Palladium(II)
Thiourea

ABSTRACT

Reaction of *N*-phosphorylated thioureas of common formula RNHC(S)NHP(O)(O*i*Pr)$_2$ (R = *t*Bu, **HL**^{I}; R = Ph, **HL**^{II}; R = 4′-benzo-15-crown-5, **HL**^{III}) with Pd(PhCN)$_2$Cl$_2$ in acetonitrile leads to complexes of the structure Pd(**HL**^{I}-*S*)$_2$Cl$_2$ (**1**), Pd(**HL**^{II}-*S*)$_2$Cl$_2$ (**2**) and Pd(**HL**^{III}-*S*)$_2$Cl$_2$ (**3**). Reaction of *N*-phosphorylated thioureas of common formula RC(S)NHP(O)(O*i*Pr)$_2$ (R = Et$_2$N, **HL**^{IV}; R = morpholine-*N*-yl, **HL**^{V}) in the same conditions leads to complexes Pd(**L**^{IV}-*O*,*S*)$_2$ (**4**) and Pd(**L**^{V}-*O*,*S*)$_2$ (**5**), where the palladium(II) atoms are coordinated in a square-planar fashion by the C=S sulfur atoms and the P=O oxygen atoms of two anionic ligands. The crystal structure of complex **1** has been investigated by X-ray crystallography. It was established that the thiourea ligands are in a *trans*-configuration and the palladium(II) cation is coordinated by the sulfur atoms of the C=S groups and the chlorine atoms. Complex **1** is the first example of palladium(II) complex in which the potentially chelating *N*-phosphorylated thiourea ligand is bound through the sulfur atom only.

1. Introduction

The coordination chemistry of polyfunctional ligands, capable to realize different coordination modes with metal cations [1] is of interest for synthesis of new selective complexing agents and analytical reagents. Koch and others have shown that the coordination of *N*,*N*-dialkyl-*N*′-aroylthioureas leads to bidentate-*O*,*S*-coordination to Pd(II) [2,3]. It was also shown that the coordination mode of *N*-alkyl-*N*′-aroylthioureas depends on an intramolecular hydrogen bond between the donor oxygen atom of the carbonyl group and the hydrogen atom of the NH group [2].

We have become interested in the coordination chemistry of *N*-phosphorylated thioureas RR′NC(S)NHP(O)(O*i*Pr)$_2$ (R = R′ = alkyl; R = H, R′ = alkyl, aryl) towards various transition metal cations [4] in view of their application in metals separation [5]. Recently, we reported, that in the square-planar complexes of *N*-phosphorylthioureas M[RNHC(S)NP(O)(O*i*Pr)$_2$]$_2$, where (M = Ni(II), R = Ph [6], *p*-MeOC$_6$H$_4$, *p*-BrC$_6$H$_4$, *t*Bu, *i*Pr, *c*-Hex [7]; M = Pd(II), R = Ph [6], *i*Pr [7]; M = Cu(II), R = Ph, *c*-Hex [6]), 1,3-*N*,*S*-coordination of the anionic ligand is realized.

Recently, we reported some synthetic results presented here as a preliminary communication [8]. Herein, we report the comparative study on the complexes of the Pd(II) ions with *N*-phosphorylthioureas, containing secondary (Scheme 1) and tertiary (Scheme 2) nitrogen at the *N*-thioacylamidophosphate moiety C(S)NHP(O)(O*i*Pr)$_2$. The crystal structure of *trans*-Pd(HL^{I}-*S*)$_2$Cl$_2$, the first example of *N*-phosphorylthiourea coordinated to Pd(II) only through the S atom in the monodentate fashion, is also reported.

2. Experimental

2.1. Synthesis of HL^{I}–HL^{V}

N-Diisopropoxyphosphorylthioureas were prepared according to the previously described methods [9].

2.2. Synthesis of **1**–**5**

A portion of Pd(PhCN)$_2$Cl$_2$ (0.192 g, 0.5 mmol) dissolved in 30 mL of acetonitrile was added dropwise to 30 mL of a well stirred solution containing **HL**$^{I–V}$ (0.296, 0.316, 0.506, 0.295 or 0.310 g; 1 mmol) in the same solvent. The mixture was stirred at room temperature for a further 10 h. The solvent was then removed *in vacuo*. A precipitate was isolated from dichloromethane by *n*-hexane.

2.2.1. Pd(HL^{I}–*S*)$_2$Cl$_2$ (**1**)

Yield: 0.331 g (86%). M.p. 128–129 °C. ^{1}H NMR (CDCl$_3$): δ 1.38–1.43 (m, 12H, CH$_3$), 1.49–1.53 (m, 9H, CH$_3$, *t*Bu), 4.58–4.73 (m, 2H,

* Corresponding author. Fax: +7843 254 37 34.
E-mail address: damir.safin@ksu.ru (D.A. Safin).

0277-5387/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.poly.2008.03.012